

**SEM MICROANALYSIS TECHNIQUES IN DEMONSTRATION OF  
SULFUR CAPTURE BY SLAG AND SORBENTS DURING  
GASIFICATION OF COAL IN A TEXACO GASIFIER**

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Slag, In-Situ Desulfurization in Coal Gasification

**ABSTRACT**

In Texaco's Coal Gasification Process, a significant portion of desulfurization of the product gas (synthesis gas, "syngas") may be achieved by slag capture in the gasification step when various sorbents are added to the coal slurry. For example, when iron oxide is added to the coal slurry, sulfur is captured primarily in a discrete iron oxysulfide phase and to a lesser degree in the glassy silicates phase. Evidence confirming the success of the sorbents approach was gathered through high-temperature, high-pressure bench scale microreactor experiments as well as those with a pilot unit gasifier at Texaco's Montebello, CA research facility. The roles of optical and scanning electron microscopy (SEM) in discerning and analyzing the phases and obtaining approximate phase quantitation are presented.

**INTRODUCTION**

One of the most promising approaches for utilizing coal in an environmentally safe manner that has been recently demonstrated is the generation of electric power via partial oxidation of coal in an integrated gasification-combined cycle (IGCC) plant. To minimize emission of sulfur compounds, these processes typically separate the reaction step (when coal is converted to raw syngas under reducing conditions at high temperatures) from the acid gas removal step (where physical solvents are generally used to scrub hydrogen sulfide and carbonyl sulfide from the crude syngas). Currently, this approach requires cooling of the hot syngas to the low temperatures commonly needed for physical solvents and subsequent reheating of this cleaned syngas prior to its introduction into the gas turbine. Consequently, these heating and cooling cycles require significant capital investments as well as operating costs.

A potentially more efficient alternative is to combine coal gasification with the sulfur removal step in the same reaction vessel. However, the solubility of sulfur in coal slags is quite low (typically between 0.01 and 0.05 weight percent). One possible approach to enhance sulfur solubility in coal slags is the addition of sulfur-capturing sorbents along with the coal feed to the gasifier. The ideal sorbent should be an inexpensive

additive that chemically reacts with the sulfur compounds in the gas phase (primarily hydrogen sulfide with smaller amounts of carbonyl sulfide) to form a disposable sulfide or oxysulfide that is encapsulated into the resultant slag, but this additive should not cause any complications for slag removal from the gasifier.

Although iron-based compounds have been employed as sorbents, most studies have been done at the lower temperatures encountered in a fluidized bed combustion or an external desulfurization process. In-situ desulfurization has not yet been demonstrated on a commercial scale with any gasification process.

To rapidly screen iron oxide as a sorbent for sulfur capture prior to its being tested in the pilot gasification unit, tests were performed in an experimental bench scale unit<sup>1,2</sup> to estimate the solubility of sulfur in a given coal slag with and without added iron as a solvent. Typical experimental SEM/EDX microanalysis data from bench-scale drop tube furnace runs with coal slag using iron oxide as an additive under simulated Texaco coal gasifier syngas compositions are presented for comparison with SEM/EDX data on slags generated from the pilot gasifier unit.

#### EXPERIMENTAL

##### SLAG SAMPLES PREPARATION

The solidified slag droplets from the drop tube furnace runs and the gasifier slag particles were prepared for polarized light microscopy studies and SEM/EDX microanalysis by encapsulating them in epoxy binder and polishing the 1-inch dia. specimen to reveal the typical particle cross sections for analysis. For SEM/EDX microanalysis the polished specimens were affixed to SEM mounts and carbon coated to render the surface conductive, thereby minimizing charge buildup by the electron beam.

##### SCANNING ELECTRON MICROSCOPE

Amray 1645 SEM equipped with: 1) lanthanum hexaboride (LaB6) electron emitter source, 2) imaging detectors for secondary as well as backscattered electrons and 3) interfaced with the EDX X-ray equipment for normalized elemental analysis for sodium ( $Z=11$ ) and elements of higher atomic number, element mapping and digital image acquisition. The analysis regime used 20 KV acceleration voltage, as well as a working distance of 24 or 35mm and zero tilt for the specimen.

##### ENERGY DISPERSIVE X-RAY ANALYSIS SYSTEM

Tracor Northern TN-5500 EDX Microanalysis System equipped with a Si(Li) semiconductor detector, LSI 11/73 CPU with 3 MByte working memory and 30 MByte mass storage capacity to record and process multielement spectra, acquire and store digital element

distribution maps and digital images. Following element mapping performed for as many as 14 elements simultaneously, the XPHASE routine was used to obtain 4-element correlations (16 combinations) pertinent to estimating phase areas. For more recent samples, an upgrade to the system also permitted estimation of the oxysulfide phase by using the distribution of contrast levels (0-255) in the 512 x 512 pixel image (Figure 4).

The EDX spectra leading to numerical elemental analyses were obtained by electron beam excitation of specific phases. Features of size 10  $\mu\text{m}$  or less were generally analyzed at 5000x and minimum partial field or in spot mode to obtain spectra from a small region of approx. 2  $\mu\text{m}$  dia. The spectra stored to disk were processed to numerical results using EDX standardless software routines and ZAF interelement correction procedures. Polished mineral standards purchased from Biorad Polaron were used to estimate element biases in the normalized results. For this report, silicon results were approximately 10 percent high (relative) when measured with aluminosilicates. Iron disulfide proved to be 0.7 percent high in sulfur and 8 percent low for iron as suggested by the spectra typical of Figure 2.

#### RESULTS OVERVIEW

SEM/EDX microanalysis techniques have contributed considerably to evaluating the success of both the bench scale desulfurization experiments and the pilot unit gasifier runs.

In the bench-scale drop furnace equilibrium type experiments the slag product available for analysis was limited to about 100 mg. In spite of this constraint, the high magnification/analysis capability allowed intimate insight into the manner in which the sulfur containing gases combined with the sorbent-slag melt to form the expected iron oxysulfides. In this connection the EDX standardless analysis methods were sufficient to give reasonable confirmation that the slag capture product was one in which the Fe/S atom ratio was close to unity (Figures 1, 2). This capability also documented the occasional reduction of the iron oxide to metallic iron where gas partial pressures and temperature conditions favored it (Figure 1 and Table I).

When applied to slag materials from pilot unit gasifier runs, the SEM/EDX microanalysis technique was able to document that sulfur capture takes place not only in the sulfide phase but also in the silicates phase as may be seen from the Table I comparison of gasifier experiments with and without sorbent on both medium-sulfur and high-sulfur coals. Although not documented here, SEM microanalysis methods are also useful for: 1) identifying phases that inhibit slag flow, 2) judging the amount of sorbent to be added to the coal prior to gasification, and 3) evaluating gasifier parameters such as temperature and slag droplet residence time.

Even without detailed microanalysis, the simple low magnification backscattered electron detector image of coal slag particle arrays immediately informs the viewer on the extent of sulfur capture. Without the use of the iron oxide sorbent only occasional miniscule iron sulfide phases are observed. When sorbent is used the iron oxysulfide phase is very visible during SEM exploration of the sample as well as in the BSED images (Fig. 3). Multielement mapping correlations and stored image analysis (Figure 4 and Table I) give numerical expression to the estimate of sulfur capture. Our recent upgrade that allows stored image analysis also permits analysis of up to 100 operator selected points per study field; this gives us the potential to determine particle-to-particle variations in both the silicate and iron oxysulfide phases. Post-SEM evaluations of the analysis files easily allow grouping and averaging of the results for a given phase.

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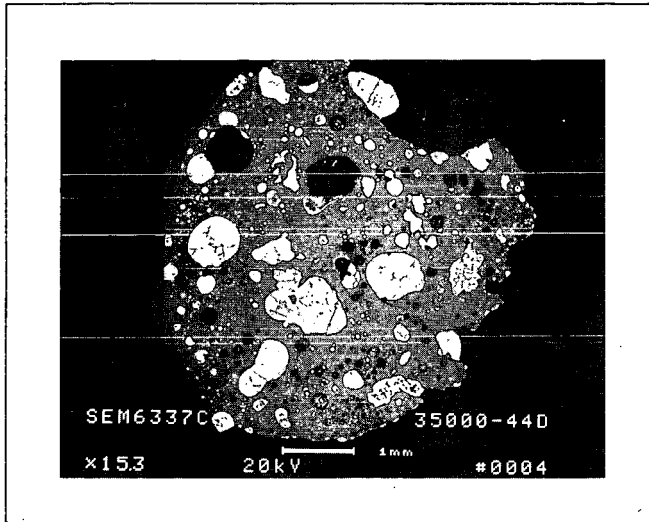
#### REFERENCES

1. A. M. Robin, C. M. Wu, and M. S. Najjar, "Integration and Testing of Hot Desulfurization and Entrained Flow Gasification For Power Generation Systems", Proceedings of the Eighth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, DOE/METC-88/6092, May, 1988.
2. M. S. Najjar, D. Y. Jung, A. M. Robin, Poster Presentation, "Theoretical Calculations and Bench-Scale Test Results of Sulfur Capture in Coal Slags Under Partial Oxidation Conditions", Third International Conference on Processing and Utilization of High-Sulfur Coals, Iowa State University, 11/15/89.

TABLE I.  
-- COAL SLAG CHARACTERIZATION --  
USING SEM/EDX MICROANALYSIS

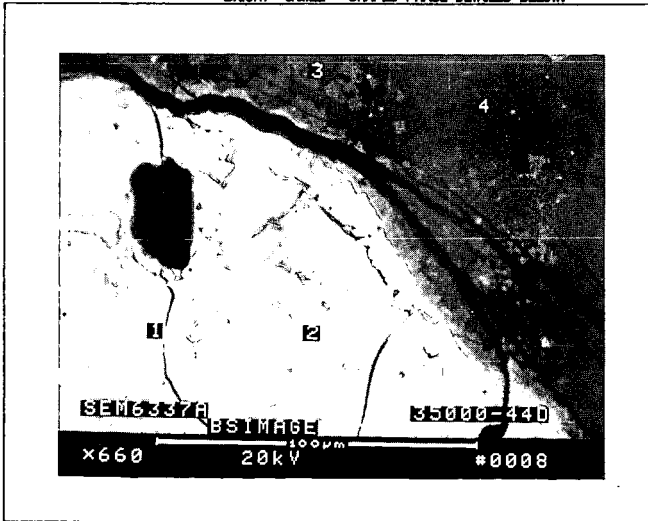
EXPERIMENT	SORBENT	COAL	SLAG PHASE	KEY ELEMENTS BY EDX (WT%)			KEY WT OR (ATOM)RATIO	PHASE AREA(%)
				SI	S	FE		
Drop Tube Furnace 35000-44D	Iron	Med S	Metallic Fe	0.5	0.2	97.9	— —	12
			Silicate	47.7	0.4	6.0	Fe/Si 0.17	87
			Oxysulfide	1.8	30.7	62.6	Fe/S (1.17)	21
Gasifier 88-MRL-67	None	Med S	Silicate	39.1	0.4	28.4	Fe/Si 0.73	Major
			Oxysulfide	1.7	28.7	68.5	Fe/S (1.42)	Trace
Gasifier 88-MRL-70	Iron Oxide	Med S	Silicate	15.7	4.4	85.8	Fe/Si 4.17	Major
			Oxysulfide	3.2	15.4	78.2	Fe/S (2.83)	Minor
Gasifier 89-MRL-58	None	HighS	Silicate	37.8	0.9	32.3	Fe/Si 0.85	96.7
			Oxysulfide	0.4	35.8	80.9	Fe/S (0.98)	1.3
Gasifier 89-MRL-63	Iron Oxide	HighS	Silicate	24.5	3.5	51.8	Fe/Si 2.11	89.5
			Oxysulfide	0.8	27.2	68.9	Fe/S (1.45)	30.5

FIGURE 1  
DROP TUBE FURNACE SLAG



SEM 6337C

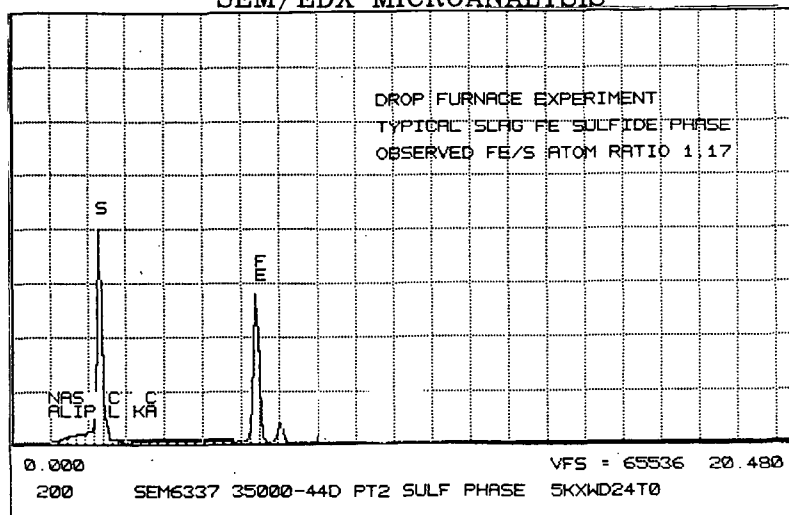
BACKSCATTERED ELECTRON IMAGE OF OVERALL PARTICLE FROM DROP TUBE FURNACE EQUILIBRIUM OF MED-SULFUR COAL SLAG AND SULFUR CONTAINING GASES. SUBJECTED TO SEM/EDX MULTIELEMENT ANALYSIS & MAPPING SUMMARIZED IN TABLE I. BRIGHT "CAMEL"-SHAPED PHASE DETAILED BELOW.



SEM 6337A

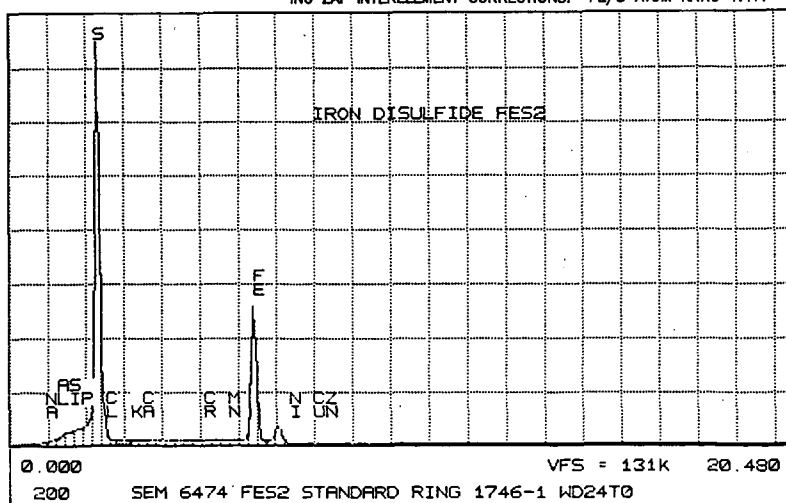
P1 - METALLIC FE. P2 - SULFIDE PHASE FE/S WT RATIO 2.04, AND FE/S ATOM RATIO 1.17. P3 - AL-FE PHASE FE/AL RATIO 0.86. P4 - SILICATE MATRIX FE/SI WT RATIO 0.17.

FIGURE 2  
SEM/EDX MICROANALYSIS



EDX SPECTRUM  
OXYSULFIDE PHASE

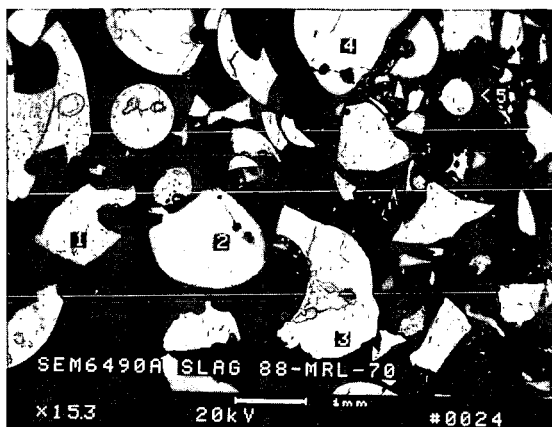
OBTAINED FROM PHASE AT POINT 2 IN SEM 6337A (FIGURE 1).  
EXHIBITING SULFUR AND IRON, SPECTRUM WAS CONVERTED TO  
NUMERICAL VALUES BY STANDARDLESS QUANT METHODS EMPLOY-  
ING ZAF INTERELEMENT CORRECTIONS. FE/S ATOM RATIO 1.17.



EDX SPECTRUM  
IRON DISULFIDE

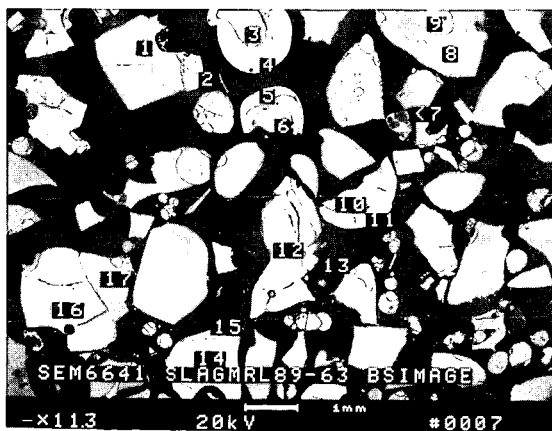
FES<sub>2</sub> MINERAL (POLISHED IN POLARON ANNULAR STD 1746-1).  
THEORETICAL FE/S ATOM RATIO OF 0.50. CONVERSION OF  
SPECTRUM GIVES OBSERVED FE/S ATOM RATIO 0.46.

FIGURE 3  
SLAGS FR COAL GASIFICATION W/IRON OXIDE



SEM 6490A, SLAG  
MED-SULFUR COAL

PARTICLES FROM GASIFICATION OF MED-SULFUR COAL. PARTICLES 1, 3, 5 HAVE OXYSULFIDE PHASES; OXYSULFIDE PHASE FOR #1 GIVES OBS. FE/S ATOM RATIO 2.8 (TABLE 1). PHASES 2, 4 ARE TYPICAL OF SILICATES AND CONTAIN AL, SI, S, CA, FE (PHASE 2 GIVES FE/SI WT RATIO 4.17).



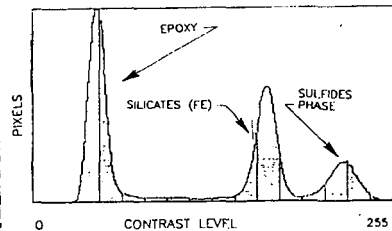
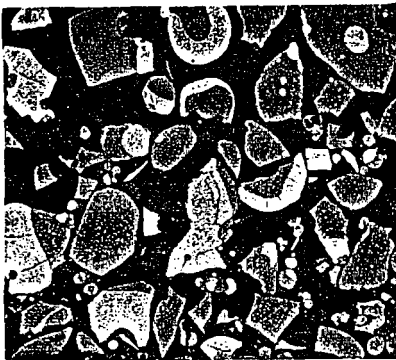
SEM 6641 SLAG  
HIGH-SULFUR COAL

AVERAGING ANALYSES FOR 8 OXYSULFIDE PHASES GIVES FE/S RATIO OF 1.45 (TABLE 1). OXYSULFIDE PHASE ESTIMATED BY ELEMENT MAPPING IS 31.9%, BY STORED IMAGE ANALYSIS 30.8% (TBL 1, FIG. 4).



FIGURE 4.

PHASE QUANTITATION BY STORED IMAGE ANALYSIS  
USING SEGMENTED CONTRAST



DISTRIBUTION FOR PIXELS IN STORED IMAGE

PHASE/FEATURE	-- IMAGE PIXELS (512 X 512 ARRAY) --		
	CONTRAST LEVEL	OBSERVED%	NORMALIZED%
EPOXY	0- 79	46.7	--
AL-SI (LOW-FE)	80-139	3.3	6.2
AL-SI-S-CA-FE	140-189	33.8	63.3
FE-S OXYSULFIDE	190-255	16.3	30.5